

Effects of Gypsum Addition on Solubility of Nutrients in Soil Amended With Peat

Moustafa A. Elrashidi, Larry T. West, Cathy A. Seybold, Ellis C. Benham, Philip J. Schoeneberger, and Richard Ferguson

Abstract: It is widely accepted that the accumulation of gypsum in gypsiferous soils results in very low fertility, even with application of fertilizers and organic amendments. The objectives were to investigate, in laboratory experiments, the effect of gypsum on the solubility of 13 nutrients and how amending the soil with organic peat moss may mitigate the impact of gypsum on nutrients and soil fertility. A 100-g sample of gypsum-free soil (Sharpsburg Fine, montmorillonitic, mesic Typic Argiudolls) was treated with increasing amounts of gypsum (0, 1, 5, 10, 15, 20, 30, and 50 g), then water was added to the mixtures to reach 50% of the water saturation capacity. Another set of soil/gypsum mixtures received 5-g peat to study the effect of peat application. All mixtures were incubated at 32°C for 15 weeks. After incubation, the concentration of water-soluble nutrients was measured. In general, the addition of gypsum increased the solubility of N, K, Ca, Mg, Mn, Cl, and S, whereas it decreased the solubility of P, Na, Fe, Cu, Zn, and B. The application of peat increased the solubility of all nutrients investigated, except for N and S. Chemical reactions and mechanisms were applied to interpret the effects of both gypsum and peat treatments on nutrient solubility and their relationship to soil fertility and crop production. The application of peat improved the solubility of most nutrients and proved to be useful as an amendment for gypsum-rich soils and increases its productivity.

Key words: Gypsiferous soils, peat moss, nutrients, incubation.

(*Soil Science* 2010;175: 162–172)

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is one of the most commonly occurring sulfate minerals in soils. It may be present in trace amounts in soils or dominate the pedon as in gypsiferous soils with a gypsic or petrogypsic horizon (Eswaran and Zi-Tong, 1991). Gypsiferous soils are most common in arid and semiarid areas where rainfall is too low to remove the gypsum from the soil profile.

During the last three decades, there has been a rapid expansion of agricultural activities into arid and semiarid areas of the United States. The application of sprinkler irrigation provides a cost-effective use of meager natural water resources. Large tracts of these areas are reclaimed and used for pasture and crop production. Kovda (1954) considers that the accumulation of gypsum in soils results in very low fertility and that their productivity remains low under irrigation, even with application of fertilizers and organic manures. The potential productivity of gypsiferous soils is related to the fact that gypsum mineral surfaces have no charges that attract exchangeable cations. Furthermore, the mineral supports high concentrations

of calcium (Ca) and sulfate ions in soil solution (Elrashidi et al., 2007), which may negatively affect the solubility of other essential nutrients such as phosphorus, iron (Fe), and manganese (Mn) in the soil (Lindsay, 1979). Moreover, the high salinity in soil may have physiological effects on reducing nutrient uptake and plant growth.

Essential nutrients for higher plants include carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), sulfur (S), potassium (K), Ca, magnesium (Mg), Fe, Mn, copper (Cu), zinc (Zn), molybdenum (Mo), boron (B), and chloride (Cl^-) (Mengel and Kirkby, 1982). Sodium (Na) has not been established as an essential nutrient for all higher plants. Carbon, H, and O are taken up by plants in the form of CO_2 gas and water; the rest of the nutrients are mainly taken as inorganic chemicals (ions) from soil and/or water.

Understanding the effect of gypsum content on the solubility of essential plant nutrients is important in determining the potential productivity of gypsum-rich soils. Most studies on gypsiferous soils have measured nutrient uptake by plants as an indicator of the effect of gypsum application on different element concentrations in soil solution. Few studies have investigated the effect of gypsum directly on the concentration of elements in soil solution. The application of organic materials, such as peat or animal manure, can mitigate the negative impact of gypsum on soil fertility and improves soil productivity. Furthermore, the presence of organic materials in soils enhances the growth of microorganisms that affect element concentration in soils through various chemical reactions/processes: (i) enhancing the bioaccumulation of cellular organic forms of elements, (ii) releasing organic acids and chelating compounds that dissolve inorganic minerals, and (iii) increasing the formation of element-organic complexes (Stevenson, 1991; Elrashidi et al., 1999). The application of peat can also improve physical properties of soil that have positive effects on soil fertility and crop productivity. However, in this research, we only investigated the effects of gypsum and peat on the solubility of nutrients in noncalcareous soils.

The objectives of this study were to investigate (in laboratory experiments) (i) the effects of increasing levels of gypsum on the solubility of 13 nutrients (N, P, K, Na, Ca, Mg, Fe, Mn, B, S, Cl, Cu, and Zn) in soil and (ii) how the application of peat moss may mitigate the negative impact of gypsum on the solubility of these elements in soil.

MATERIALS AND METHODS

Effect of Gypsum and Peat on Nutrients

The effect of gypsum on nutrient solubility in soil was investigated in a laboratory experiment. An air-dried less than 2-mm gypsum/calcite-free soil (Sharpsburg Fine, montmorillonitic, mesic Typic Argiudolls) was used. A 100-g soil sample was treated with increasing amounts (0, 1, 5, 10, 15, 20, 30, and 50 g) of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, analytical reagent) in separate 250-mL plastic beakers. The required amounts of soil and

USDA/NRCS, National Soil Survey Center, 100 Centennial Mall North, Lincoln, NE 68508. Dr. Moustafa Elrashidi is corresponding author. E-mail: moustafa.elrashidi@lin.usda.gov

Received February 2, 2010, and in revised form March 5, 2010.

Accepted for publication March 10, 2010.

Copyright © 2010 by Lippincott Williams & Wilkins

ISSN: 0038-075X

DOI: 10.1097/SS.0b013e3181dd51d0

gypsum were mixed thoroughly, and then deionized water was added to the mixture to reach 50% of the water saturation capacity. The water saturation capacity (%) was predetermined in a separate sample for all mixtures. Three replicates were used for each treatment, which gave a total of 24 soil/gypsum mixtures.

Another set of identical 24 soil/gypsum mixtures was prepared for studying the effect of peat application on the water solubility of elements. An air-dried finely ground (<2-mm) sphagnum peat moss was used. A 5-g peat sample was added to each of the 24 soil/gypsum mixtures. The materials were mixed thoroughly before adding distilled water to reach 50% of the water saturation. The water saturation capacity (%) was predetermined in a separate sample for all mixtures.

The 48 mixtures were incubated in a well-aerated oven at 32°C (90°F) for 15 weeks. The water was added weekly to compensate for any loss caused by evaporation and to keep the moisture content constant at the 50% level. At the end of the incubation period, the mixtures were air-dried and crushed to pass through a 2-mm sieve before analysis.

Analyses of Soil/Gypsum/Peat Mixtures

Soil properties were determined on the air-dried less than 2-mm sample by methods described in Soil Survey Investigations Report No. 42 (USDA/NRCS, 2004). Alphanumeric codes in parentheses next to each method represent specific standard operating procedures in the report. Particle size analysis was performed by sieve and pipette method (3A1). Cation exchange capacity (CEC) was conducted by NH₄OAc buffered at pH 7.0 (5A8b). Exchangeable Ca, Mg, K, and Na were determined by NH₄OAc buffered at pH 7.0 (4B1). Total C content was determined by dry combustion (6A2f), and CaCO₃ equivalent was estimated by electronic manometer method (6E1g). Soil pH was measured in a 1:1 soil/water suspension (8C1f). Clay minerals were identified by the X-ray diffraction (7A1a1). Water saturation (%) was estimated by the saturated soil paste method (4F2). With respect to the peat sample, the total C content was determined by dry combustion (6A2f).

The water-soluble elements in the soil, gypsum, peat, and mixtures were determined according to the Soil Survey Laboratory procedure (4D2b1) (USDA/NRCS, 2004). In this method (4D2b1), the soil-water suspension (20 g of soil and 100 mL of distilled water) was allowed to equilibrate at room temperature for 23 h. The suspension was then shaken for 1 h. The supernatant was passed through a 0.45-μm filter. Elements (P, K, Na, Ca, Mg, Fe, Mn, Cu, Zn, and B) were determined in the filtrate by inductively coupled plasma-optical emission spectrometry (Perkin Elmer 3300 DV). Nitrate (NO₃-N), sulfate (SO₄²⁻), and chloride (Cl⁻) concentrations in the filtrate were determined by the high-pressure ion chromatograph (6M1c) (Dionex Corporation, Bannockburn, IL). The pH in the water extract was determined by the combination electrode and digital pH/ion meter, Model 950, Fisher Scientific (8C1a). The conductivity bridge (4F1a1) was applied to measure the electric conductivity and soluble salts (EC).

RESULTS AND DISCUSSIONS

Selected properties of the gypsum/calcite-free soil sample used for this study (Sharpsburg Fine, montmorillonitic, mesic Typic Argiudolls) were as follows. The clay, silt, and sand percentages were 38.9%, 59.7%, and 1.4%, respectively. The soil pH was 6.7 for water and 6.1 in 0.01 M CaCl₂ solution. The CEC was 30.9 cmol(+)kg⁻¹, whereas the NH₄OAc-extractable Ca, Mg, Na, and K were 18.3, 7.1, 0.0, and 1.2 cmol(+)kg⁻¹, respectively. The combustion analysis conducted on the soil sample indicated that the total C and N contents were 1.96% and

0.20%, respectively. The X-ray analysis indicated that clay minerals in Sharpsburg soil include smectite and micas. The pH, EC, and the concentration of Cl, SO₄²⁻, and NO₃-N in the water extract for both the Sharpsburg soil and peat samples as well as in different soil/gypsum/peat mixtures, incubated for 15 weeks, are presented in Table 1. The concentrations of water-soluble P, K, Na, Ca, Mg, Fe, Mn, B, Cu, and Zn in the soil, peat, and mixtures are given in Table 2.

Effect on pH and EC

When gypsum is added to soil, the final soil pH may arise from two conflicting reactions between gypsum and soil surfaces. Calcium replaces both H and Al (which hydrolyzes to

TABLE 1. The AV and S.D. of the pH, EC, and Concentrations[†] of Cl, SO₄, and NO₃-N in the Water Extracts of Sharpsburg Soil/Gypsum/Peat Mixtures Incubated for 15 Weeks

Treatment [‡]	AV and S.D.	pH	EC, ohm	Cl, mg/kg	SO ₄ ²⁻ , mg/kg	NO ₃ -N, μg/kg
0	AV	7.20	0.34	19.00	14.33	390.10
	SD	0.00	0.44	1.19	0.70	87.02
1	AV	6.40	1.69	11.89	6,863.74	370.87
	SD	0.00	0.06	0.84	1,034.32	59.02
5	AV	6.37	2.40	27.38	10,802.42	852.36
	SD	0.06	0.01	3.17	211.17	119.61
10	AV	6.33	2.46	28.33	11,438.11	960.70
	SD	0.06	0.11	0.74	48.27	173.98
15	AV	6.30	2.37	28.52	10,260.05	1,026.76
	SD	0.00	0.01	6.31	84.89	103.36
30	AV	6.33	2.35	28.25	11,721.85	611.82
	SD	0.06	0.02	2.30	139.14	77.38
50	AV	6.20	2.40	28.23	12,896.73	450.95
	SD	0.10	0.11	2.50	578.67	154.25
0P	AV	6.17	0.12	19.40	95.86	345.66
	SD	0.06	0.04	1.27	73.00	91.58
1P	AV	5.40	1.60	26.93	5,467.38	291.89
	SD	0.00	0.05	11.56	177.77	14.26
5P	AV	5.40	2.46	29.73	10,343.78	477.58
	SD	0.00	0.02	2.03	20.00	76.80
10P	AV	5.33	2.40	28.07	10,892.31	459.04
	SD	0.06	0.15	0.68	42.91	54.34
15P	AV	5.30	2.35	30.05	11,230.03	501.64
	SD	0.00	0.05	1.78	52.20	132.95
20P	AV	5.30	2.32	28.81	11,960.37	473.38
	SD	0.00	0.04	1.98	81.38	44.68
30P	AV	5.40	2.31	34.32	13,093.98	479.88
	SD	0.17	0.10	2.16	407.24	117.48
50P	AV	5.43	2.11	26.07	14,157.44	453.58
	SD	0.06	0.08	9.33	397.24	224.54
Soil	AV	6.70	0.13	6.17	73.36	559.93
	SD	0.00	0.03	0.52	48.36	13.54
Peat	AV	3.80	0.41	43.35	102.69	1,060.37
	SD	0.00	0.11	1.47	12.04	80.96

[†]The concentration of nutrients was determined by using high-pressure ion chromatograph.

[‡]Numbers 0 through 50 refer to the amount of gypsum (g) added to a 100-g soil sample; P next to number refers to a 5-g peat sample added to each soil/gypsum mixtures.

AV: average.

TABLE 2. The AV Concentration and S.D. of 10 Nutrients in the Water Extracts of Sharpsburg Soil/Gypsum/Peat Mixtures Incubated for 15 Weeks

Treatment [†]	AV and S.D.	P, mg/kg	K, mg/kg	Na, mg/kg	Ca, mg/kg	Mg, mg/kg	Fe, mg/kg	Mn, mg/kg	B, µg/kg	Cu, µg/kg	Zn, µg/kg
0	AV	2.19	27.86	38.66	34.62	15.50	48.88	0.31	2,794.60	72.70	3,707.30
	SD	0.11	3.05	5.35	2.88	1.49	4.95	0.03	43.61	4.80	294.87
1	AV	1.65	163.99	11.72	1,744.35	241.65	0.00	0.67	235.16	13.97	989.13
	SD	0.12	3.86	0.20	84.89	6.23	0.00	0.09	54.57	0.48	83.97
5	AV	1.64	207.81	13.47	3,139.23	317.31	0.00	0.79	221.20	14.77	1,095.82
	SD	0.05	1.33	0.41	6.60	1.06	0.00	0.08	23.51	1.24	329.09
10	AV	1.80	210.38	16.54	3,281.99	324.65	0.00	1.02	244.68	17.12	975.00
	SD	0.21	3.59	3.16	23.06	3.55	0.00	0.13	25.94	1.60	263.11
15	AV	1.62	213.23	14.72	3,422.51	334.51	0.00	0.79	224.40	16.48	1,232.15
	SD	0.03	2.34	0.48	0.88	2.36	0.00	0.06	15.82	2.17	244.76
20	AV	1.84	220.51	14.79	3,575.58	341.44	0.00	1.06	211.64	17.36	1,271.24
	SD	0.16	0.84	0.56	25.91	3.66	0.00	0.13	34.00	1.59	216.19
30	AV	1.99	227.33	15.22	3,818.38	352.18	0.00	0.89	224.21	17.03	1,186.64
	SD	0.12	1.91	0.35	3.60	2.99	0.00	0.12	23.56	0.79	261.96
50	AV	2.31	236.02	26.63	4,363.66	377.00	0.00	0.99	232.75	17.80	2,114.60
	SD	0.08	2.52	9.55	35.41	2.30	0.00	0.12	57.69	3.23	731.03
0P	AV	2.72	52.56	34.95	56.83	27.74	74.23	2.21	3,387.62	93.28	5,005.74
	SD	0.21	9.50	8.11	16.73	6.41	15.49	1.04	811.47	9.04	320.28
1P	AV	1.77	193.50	15.15	1,734.04	260.89	0.00	44.59	393.37	21.48	1,211.72
	SD	0.11	4.58	0.22	44.96	3.71	0.00	1.23	9.46	0.93	281.84
5P	AV	1.97	241.20	16.93	3,195.94	437.78	0.00	66.43	383.39	22.48	1,572.71
	SD	0.24	0.22	1.20	14.76	0.67	0.00	2.97	37.04	1.78	214.58
10P	AV	2.09	251.40	19.25	3,379.07	387.22	0.00	69.65	353.40	23.46	1,438.04
	SD	0.15	0.22	2.52	23.98	59.68	0.00	3.07	34.72	2.19	328.93
15P	AV	2.22	255.93	22.13	3,505.29	359.11	0.02	70.03	357.80	20.76	1,773.84
	SD	0.16	2.28	6.94	33.25	3.80	0.04	3.04	16.13	0.87	525.85
20P	AV	2.55	261.22	24.83	3,662.18	367.99	0.00	77.36	395.96	25.50	2,124.08
	SD	0.16	6.66	7.50	85.56	8.29	0.00	3.72	78.77	3.03	1,097.32
30P	AV	2.53	262.44	34.86	3,915.02	382.18	0.00	70.49	325.44	28.22	3,640.41
	SD	0.31	19.75	15.00	99.73	4.53	0.00	0.98	151.31	4.56	1,470.45
50P	AV	2.86	267.34	46.38	4,580.84	423.81	0.00	81.15	300.45	43.66	4,061.78
	SD	0.31	6.97	9.85	88.57	10.39	0.00	4.40	81.43	13.18	236.22
Soil	AV	2.23	37.36	34.71	62.10	20.48	22.71	0.40	2,383.80	68.80	2,215.77
	SD	0.08	3.74	2.21	8.32	1.54	11.39	0.07	447.10	2.88	1,254.62
Peat	AV	49.38	70.31	40.42	107.07	55.59	5.89	1.46	9,786.97	29.60	4,557.17
	SD	1.00	0.61	12.11	3.15	2.05	0.31	0.06	516.72	5.57	922.03

[†]The concentration of nutrients was determined by using inductively coupled plasma–optical emission spectrometry.

[‡]Numbers 0 through 50 refer to the amount of gypsum (g) added to a 100-g soil sample; P next to number refers to a 5-g peat sample added to each soil/gypsum mixture.

AV: average.

give H^+), whereas SO_4^{2-} replaces OH by ligand exchange. The resultant pH measured will thus depend on the extents of the two reactions in any particular case. For Sharpsburg soil, which initially is slightly acidic (Table 1), thus, the first reaction should be more active.

The addition of 1 g of gypsum to a 100-g soil sample decreased the pH in the water extract by 0.8 units compared with the control, whereas increasing the amount of gypsum from 5 through 50 g decreased the pH by only 0.2 units (Fig. 1A). In a field experiment in South Central Montana, Cates et al. (1983) compared the effectiveness of both spent sulfuric acid (copper smelters waste) and gypsum for reclaiming calcareous saline sodic soils. They found that gypsum lowered pH values more

than an equivalent rate of the smelter acid. Shainberg et al. (1989) reported that the magnitude of the pH change caused by gypsum addition was usually small (0.2–0.3 pH units) and typically was not detectable in an electrolyte suspension but only when pH was measured in water.

For the soil and soil/gypsum mixtures, the application of peat decreased the pH in the water extract by about one unit regardless of the level of gypsum content (Fig. 1A). These results suggest no interactions between peat and gypsum that affect the soil pH.

Expectedly, the addition of gypsum seemed to increase the soluble salts in the soil (Fig. 1B). The addition of 1 g of gypsum to a 100-g soil sample increased the EC value in water from

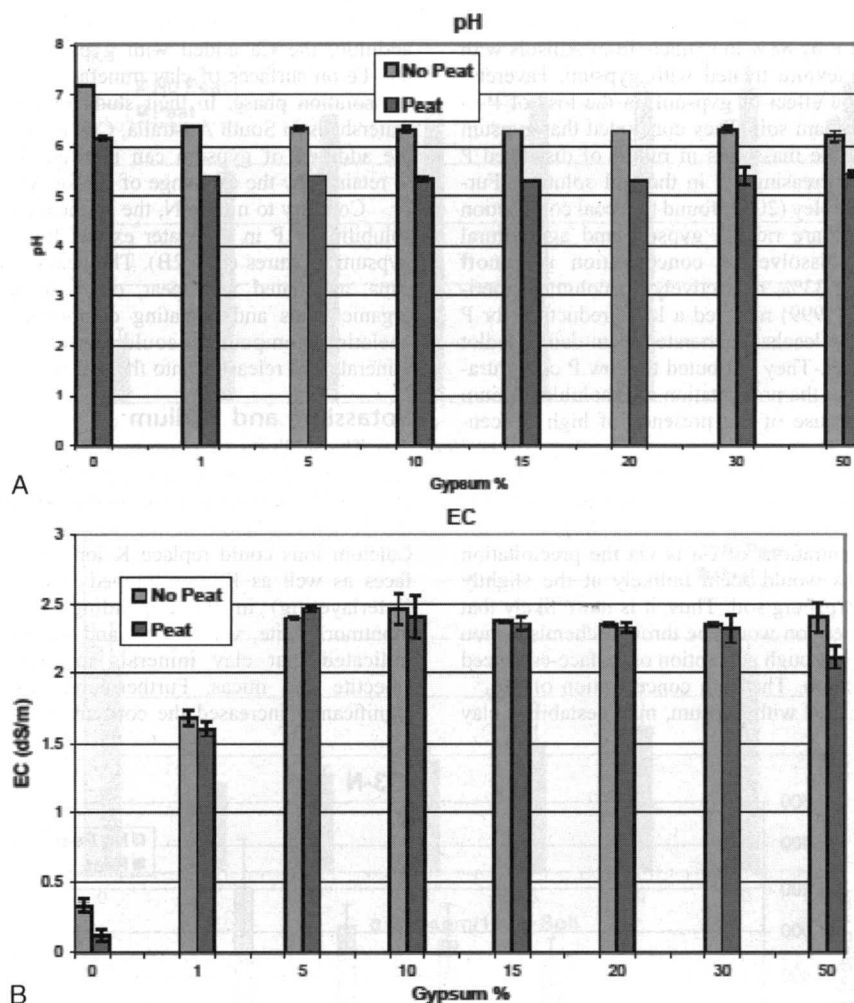


FIG. 1. Effects of gypsum and peat addition on pH (A) and EC (in dS/m) (B) in water extracts of Sharpsburg soil incubated for 15 weeks.

0.34 to 1.69 dS/m. The value of EC increased to 2.40 dS/m by the addition of 5 g gypsum, then it remained almost constant when gypsum increased from 5 through 50 g. This constant EC may suggest that the concentration of salts in these mixtures was controlled by the solubility of sparingly soluble minerals (Lindsay, 1979; Elrashidi et al., 2007).

In general, the application of peat slightly decreased the EC value in the soil and soil/gypsum mixtures relative to the no-peat samples (Fig. 1B). The sorption of ions (cations and anions) by organic matter sites could be attributed to decreasing the concentration of soluble salts in water. In addition, the formation of insoluble metal-organic complexes might decrease the amount of soluble salts and the EC value in the water extract (Stevenson, 1991; Elrashidi et al., 1999).

Nitrogen and Phosphorus

The effect of gypsum on the $\text{NO}_3\text{-N}$ concentration in water was dependent upon the amount of gypsum added to the 100-g soil sample (Fig. 2A). The addition of 1.0 g of gypsum had little effect on the concentration of $\text{NO}_3\text{-N}$, whereas increasing the added gypsum from 5 through 20 g significantly increased the concentration of $\text{NO}_3\text{-N}$. However, when the amount of gypsum in the 100-g soil sample was in excess of 20 g, the concentration of $\text{NO}_3\text{-N}$ decreased significantly. Singh and Taneja (1977) reported that the rate of N mineralization in soils is usually

stimulated by the addition of gypsum at a rate of 2.5 to 5 t/ha. However, the addition of higher rates of gypsum (7.5–10 t/ha) led to a lower level of N mineralization. It is believed that the addition of gypsum at a low rate stimulates soil microorganisms responsible for mineralization (Singh and Taneja, 1977).

The application of peat to the soil/gypsum mixtures significantly decreased the concentration of $\text{NO}_3\text{-N}$ in water (Fig. 2A). The application of organic matter usually increases the biological activity in soil and enhances the accumulation of N in cellular organic forms. In the present study, the magnitude of N immobilization by microorganisms seemed to not be significantly affected by the addition of gypsum. The positive effect of gypsum on N mineralization (Singh and Taneja, 1977) might have been overshadowed by the biological accumulation of N by microorganisms. The latter reaction was enhanced by a suitable C:N ratio in the mixtures.

In general, the addition of different amounts of gypsum to Sharpsburg soil decreased the concentration of P in water extract (Fig. 2B). The addition of high concentrations of Ca ions could contribute to the decrease in P solubility. Calcium enhances the formation of basic calcium phosphate minerals that lower the concentration of phosphate in the water extract. Larsen et al. (1965) suggested that the decrease in labile phosphate could be the result of the formation of a crystalline basic calcium phosphate at a rate that increases with increases in soil pH. In

a column-leaching study, Nelson et al. (1991) reduced the concentration of dissolved P by 88% in extracts from Alfisols with a sandy loam surface texture treated with gypsum. Faveretto et al. (2006) studied the effect of gypsum on the loss of P in runoff from Miami silt loam soil. They concluded that gypsum significantly decreased the mass loss in runoff of dissolved P and attributed that to increasing Ca in the soil solution. Furthermore, Stout and Sharpley (2000) found that coal combustion by-products (CCB) that are rich in gypsum and agricultural gypsum reduced the dissolved P concentration in runoff from soils by 43% and 33%, respectively. In column experiments, Elrashidi et al. (1999) reported a large reduction for P concentration (87.7%) in leachate generated from dairy feedlot surface treated with CCB. They attributed the low P concentration in leachate mainly to the precipitation of insoluble calcium phosphate minerals because of the presence of high concentrations of Ca in the CCB.

Moore and Miller (1994) and Coale et al. (1994) indicated that gypsum may reduce P solubility by enhancing Ca-P precipitation. A common perception of increased P sorption in the presence of high concentrations of Ca is via the precipitation of Ca phosphates. This would seem unlikely at the slightly acidic pH (6.7) for Sharpsburg soil. Thus, it is more likely that the mechanism of P retention would be through chemisorption of P on Al and Fe either through adsorption or surface-enhanced heterogeneous precipitation. The high concentration of SO_4^{2-} ions and acidity, associated with gypsum, may destabilize clay

mineral surfaces that release Al and Fe in the soil solution. In addition, the Ca added with gypsum could replace both Al and Fe on surfaces of clay minerals and releases more ions in the solution phase. In their study to reduce P in runoff from watersheds in South Australia, Cox et al. (2005) concluded that the addition of gypsum can increase the ability of the soils to retain P by the exchange of Ca for Al, Fe, and Mn.

Contrary to nitrate-N, the application of peat increased the solubility of P in the water extract for both the soil and soil/gypsum mixtures (Fig. 2B). The heavy growth of microorganisms, associated with peat, could secrete large amounts of organic acids and chelating compounds. Organic acids and chelating compounds could dissolve insoluble phosphate minerals and release P into the soil solution (Stevenson, 1991).

Potassium and Sodium

The addition of gypsum significantly increased the concentration of K in Sharpsburg soil (Fig. 3A). However, increasing the amount of gypsum did not proportionally increase the K concentration in the soil and soil/gypsum mixtures. Calcium ions could replace K ions on the exchangeable surfaces as well as K ions trapped in a nonexchangeable form (interlayering) in the expanding 2:1 clay minerals (i.e., montmorillonite, vermiculite, and micas). The X-ray analysis indicated that clay minerals in Sharpsburg soil include smectite and micas. Furthermore, the application of peat significantly increased the concentration of K in the soil and

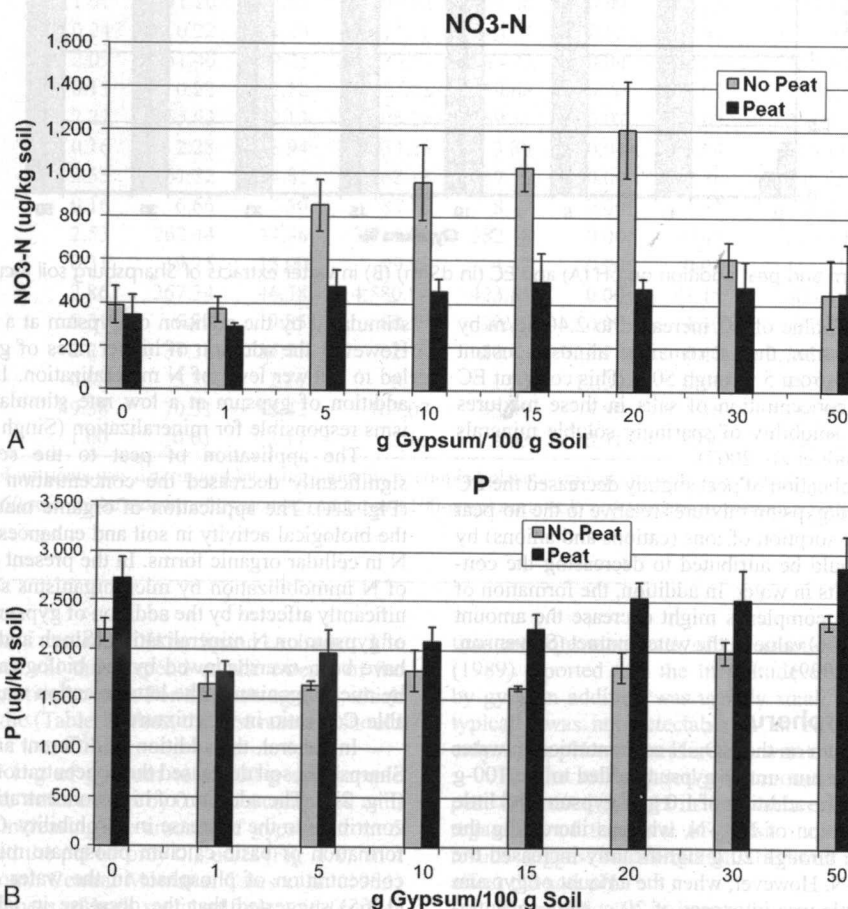


FIG. 2. Effects of gypsum and peat addition on $\text{NO}_3\text{-N}$ (A) and P (B) concentrations (in $\mu\text{g/kg}$) in water extracts of Sharpsburg soil incubated for 15 weeks.

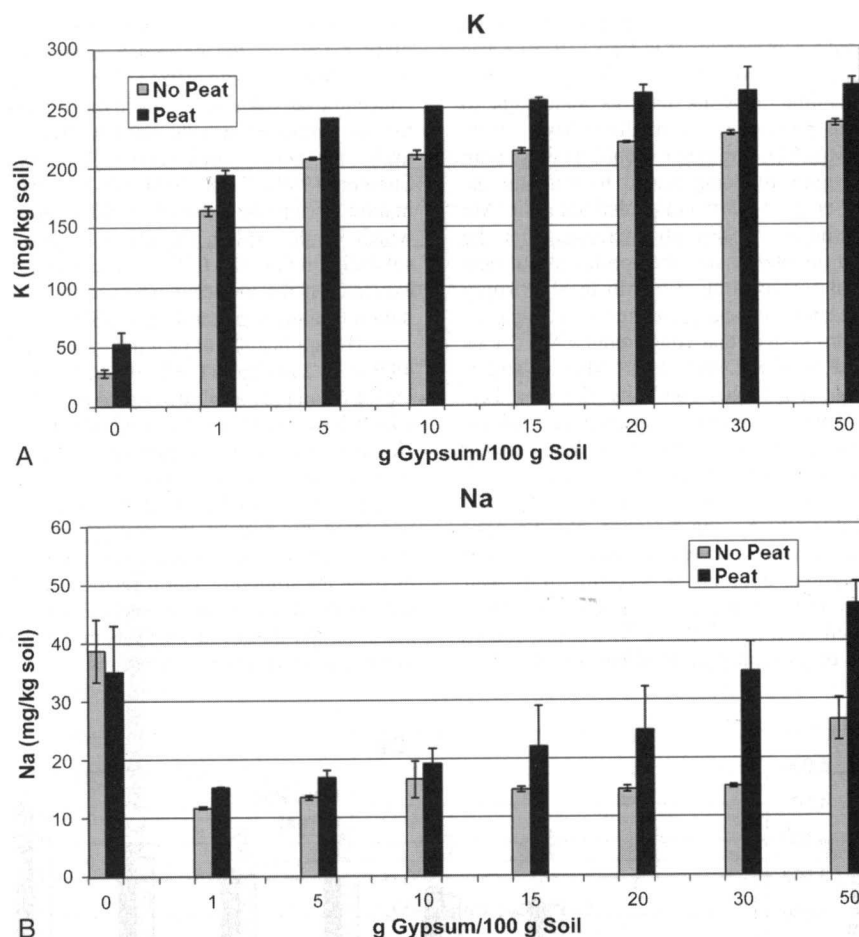


FIG. 3. Effects of gypsum and peat addition on K (A) and Na (B) concentrations (in mg/kg) in water extracts of Sharpsburg soil incubated for 15 weeks.

soil/gypsum mixtures. This could be caused by the dissolution of K-containing minerals (i.e., feldspars) by organic acids and chelating compounds. The chemical analyses of the peat sample (Table 2) indicated the presence of small amounts of nutrients including K (109 mg/kg). Thus, some of the increase in K concentration could be attributed to the additive effect (0.54 mg K/100 g soil).

Unexpectedly, the addition of gypsum seemed to decrease the concentration of Na in Sharpsburg soil (Fig. 3B). The considerable amount of SO_4^{2-} ions (added with gypsum) increased the formation of soluble NaSO_4^- species in water, which could be retained by the anion sorption sites on the clay mineral surfaces. The Sharpsburg soil has an extremely low content of Na, which is mainly present in the soil solution (actually, exchangeable Na was undetectable). This scenario made it possible for the NaSO_4^- species to play an important role in decreasing the Na ion concentration in the soil/gypsum mixtures. When soils have relatively high contents of Na, it is mainly located in the exchangeable phase. Under this condition, the added SO_4^{2-} would remove the exchangeable Na ions into the soil solution. It is likely that the exchangeable reaction could overshadow the formation of NaSO_4^- species.

Similar to K, the application of peat significantly increased the Na concentration in the soil/gypsum mixtures (Fig. 3B). Factors that contributed to the increase in K concentration could also be applied to Na. Furthermore, the rate of Na increase, as a

result of the peat application, seemed to increase by increasing the percentage of gypsum in the mixtures.

Calcium and Magnesium

Expectedly, gypsum added a considerable amount of Ca to the soil, and it increased with increasing the amount of gypsum (Fig. 4A). The application of peat raised the soil acidity (Fig. 1A), which could increase the dissolution of gypsum and Ca-containing minerals. Furthermore, a small amount of Ca might be added to the soil with the 5-g peat sample.

Meanwhile, addition of gypsum increased the magnesium (Mg) concentration in the water extract because the Ca ions added with gypsum could replace the exchangeable Mg on the clay surfaces (Fig. 4B). Shainberg et al. (1989) reported that gypsum applied at the soil surface is likely to help Ca in replacing other exchangeable cations, notably Mg, and render it prone to leaching. This depletion of Mg from the top soil can have serious consequences, particularly on sandy soils with low CEC. Similar to Ca, the application of peat significantly increased the Mg concentration in the water extract. Factors that contributed to the Ca increase as a result of the peat application could be applied to Mg.

Iron and Manganese

In general, the addition of gypsum increased the concentration of Mn in Sharpsburg soil (Fig. 5A). Under well-oxidized

conditions, Mn is present in soil as manganite (MnOOH) and/or pyrolusite (MnO_2) minerals (Lindsay, 1979). The addition of high concentrations of SO_4^{2-} to Sharpsburg soil could convert Mn-containing minerals such as manganite to $\text{Mn}_2(\text{SO}_4)_3$ where Mn is present in the oxidized Mn^{+3} form. Thus, the solubility of $\text{Mn}_2(\text{SO}_4)_3$ mineral should increase with increasing amounts of gypsum being added to mitigate the soil acidity. Shainberg et al. (1989) concluded that the Mn concentration in soil solution consistently increases after the addition of gypsum. On the other hand, the application of peat considerably increased the concentration of Mn in Sharpsburg soil (Fig. 5A). The presence of peat generates reducing conditions in the soil/gypsum system that could reduce Mn^{+3} ions in $[\text{Mn}_2(\text{SO}_4)_3]$ mineral to Mn^{+2} , such as in MnSO_4 and/or $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ that has a much higher solubility in water. Furthermore, increasing gypsum percentage seemed to increase the rate of Mn increase in the mixtures. This could be attributed to the increase in acidity with the addition of gypsum.

The concentration of water-soluble Fe was about 49 mg/kg in Sharpsburg soil (Table 2). As can be seen, the Fe concentration in water was below the detection limit for all soil samples treated with various amounts of gypsum. It is well known, however, that Fe presents mainly in the high oxidation Fe^{+3} form in well-aerated soils (Lindsay, 1979). As previously mentioned, the addition of gypsum decreased the soil pH value

by about one unit (Fig. 1A), which could increase the sorption of Fe^{+3} ions on the colloidal oxide/hydroxide and clay mineral surfaces (Sposito, 1985). Furthermore, the addition of high concentrations of SO_4^{2-} ions in the presence of K could enhance the formation of jarosite mineral $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ in soils under the acidic environment (Lindsay, 1979; O'Brien and Sumner, 1988). Thus, both the Fe sorption reaction and formation of jarosite mineral could remove Fe^{+3} from solution, which would explain the effect of gypsum on decreasing Fe solubility in this soil. O'Brien and Sumner (1988) gave a similar explanation for lowering Al concentration through the precipitation of alunite mineral $[\text{KAl}_3(\text{SO}_4)(\text{OH})_{10}]$.

The application of peat increased the Fe concentration from 48.9 to 74.2 mg/kg in the Sharpsburg soil sample (Table 2). This increase could be attributed to the reduction of Fe^{+3} to Fe^{+2} ions, which have much higher solubility in water (Lindsay, 1979). However, the addition of gypsum decreased the Fe concentration in water below the detection limit for all soil samples treated with peat. One should have expected that the low redox potential generated by peat in the soil/gypsum mixtures would result in the formation of considerable amounts of ferrous ions and increase the solubility. But it seemed that the formation of insoluble ferric sulfate mineral, such as jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ might be the dominant mechanism controlling the Fe solubility in these soil/gypsum/peat mixtures.

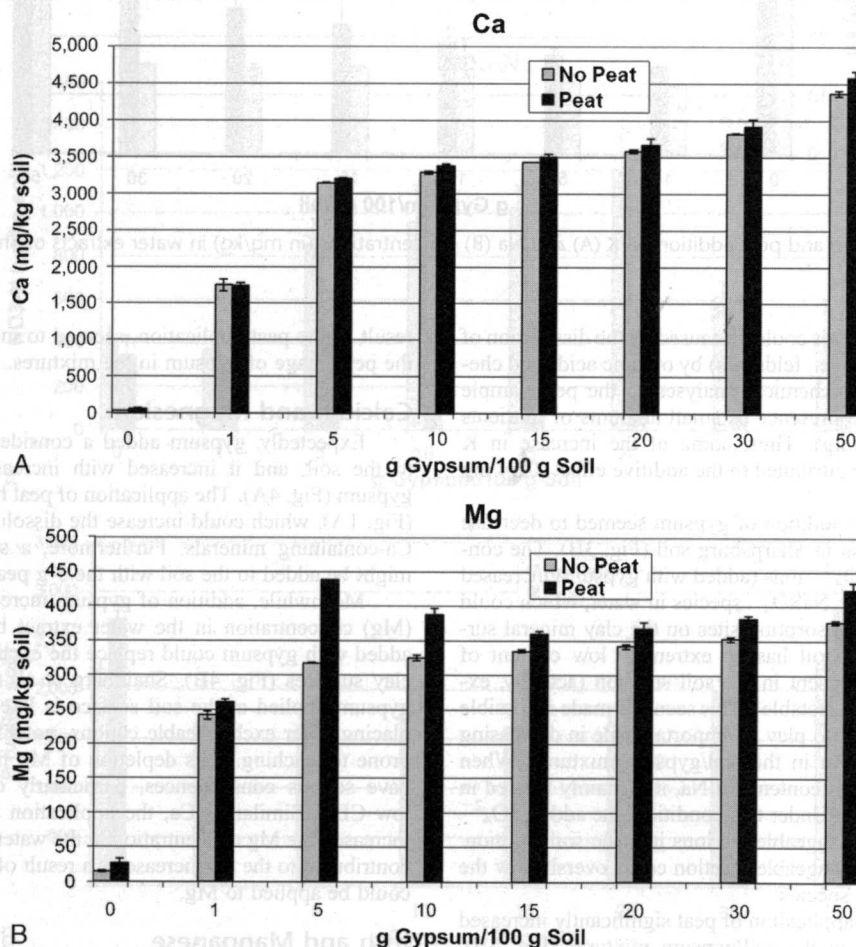


FIG. 4. Effects of gypsum and peat addition on Ca (A) and Mg (B) concentrations (in mg/kg) in water extracts of Sharpsburg soil incubated for 15 weeks.

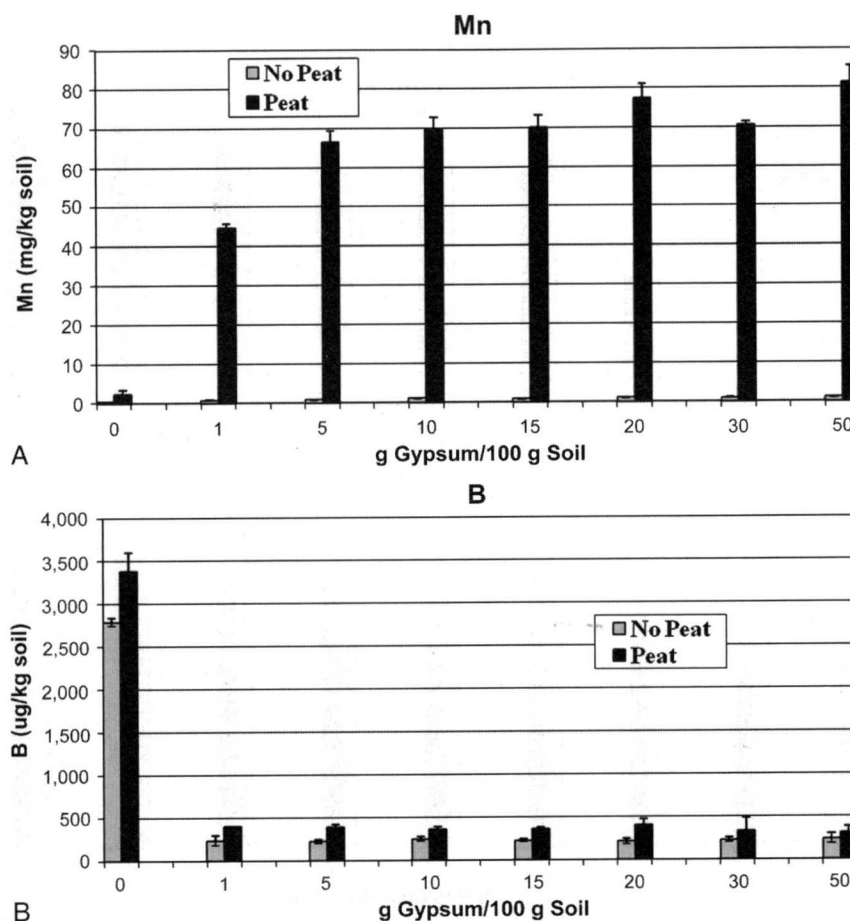


FIG. 5. Effects of gypsum and peat addition on Mn (A) (in mg/kg) and boron (B) (in µg/kg) concentrations in water extracts of Sharpsburg soil incubated for 15 weeks.

Boron

The data indicate that the addition of gypsum significantly decreased the concentration of B in Sharpsburg soil and soil/peat mixtures (Fig. 5B). Increasing gypsum addition from 1 through 50 g/kg soil did not change the decreasing rate of B in soil. In field studies conducted on sandy loam soil, Carter and Cutcliffe (1990) found that addition of gypsum decreased B concentration in the leaf tissue of Brussels sprouts as the soil pH level decreased. The addition of gypsum introduces high concentrations of SO_4^{2-} ions and associated acidity, which can destabilize clay mineral surfaces and expose new sorption sites. This process could increase B sorption by clay minerals in soil. Furthermore, the salinity introduced to soil with gypsum addition (Fig. 2) could also increase B sorption. Fleet (1965) and Couch and Grim (1968) concluded that the increased B sorption with salinity may be caused by increased dissociation of H_3BO_3 caused by salt effects. Another explanation for the negative effect of gypsum on B concentration could be related to the large amount of Ca added with gypsum. Calcium ions attached to clay minerals could enhance B sorption by acting as a bridge between clay surfaces and H_2BO_3^- ions (Elrashidi and O'Connor, 1982; Keren, 1996).

The application of peat (5 g/100-g soil) increased the B concentration in Sharpsburg soil (from 2.80 to 3.39 mg/kg soil; Table 2). The 5-g peat sample had approximately 0.5 mg B, which implies that a large portion of this increase could be

attributed to the addition of B with the 5-g peat sample. Interactions between peat organic compounds and soil minerals could be another mechanism contributing to the increased B. Organic acids and chelating compounds could dissolve minerals (i.e., tourmaline) and release B into the soil solution (Stevenson, 1991).

Sulfur and Chloride

Expectedly, the addition of gypsum considerably increased the concentration of SO_4^{2-} in the soil investigated (Fig. 6A). In a 2-year field experiment, Zheljazkov et al. (2006) reported that gypsum application on dykeland soil increased dry matter yields and Mehlich3-extractable S and S uptake by plants.

The effect of peat application on the concentration of SO_4^{2-} seemed to be dependent upon the amount of gypsum added to the soil. The application of peat decreased the concentration of SO_4^{2-} when the gypsum rate was 10 g/100 g soil or less while increasing the concentration in the soil sample when the gypsum addition was above that rate. In Louisiana, Viator et al. (2002) found that subsoil and within-row application of gypsum and compost increased leaf S concentration of sugarcane grown on a silty clay loam soil.

The decrease in the concentration of SO_4^{2-} could be attributed to the increase in the activity of microorganisms in the soil and/or the conversion of some sulfate to sulfide caused by the low redox potential (Lindsay, 1979). On the other hand,

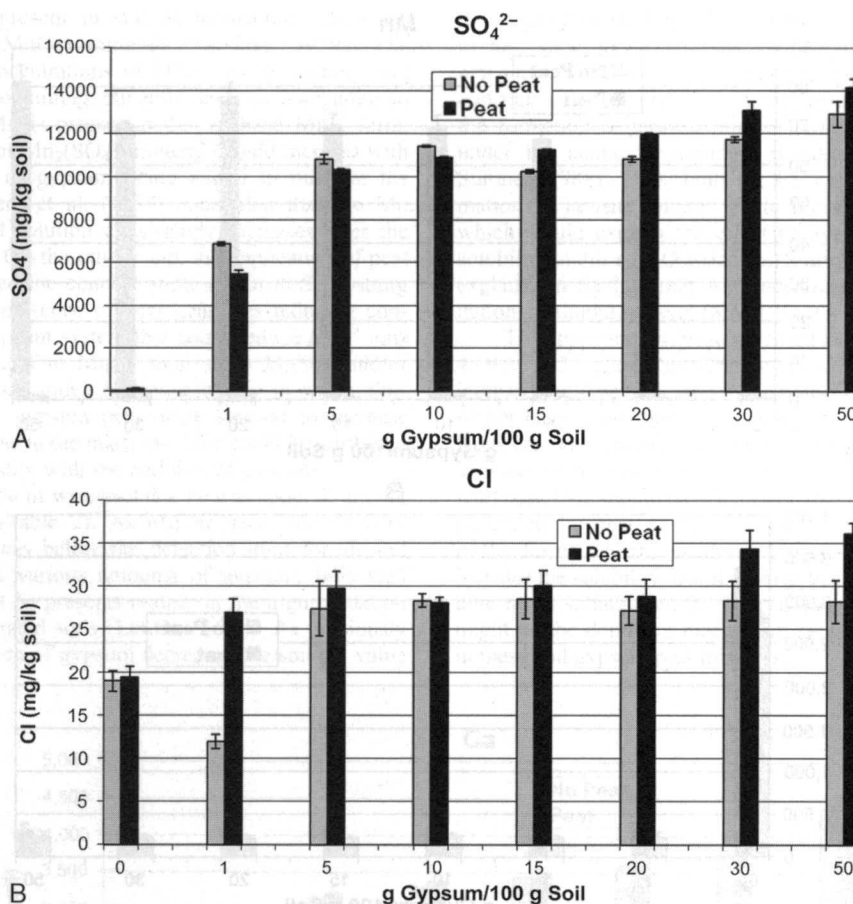


FIG. 6. Effects of gypsum and peat addition on SO₄ (A) and Cl (B) concentrations (in mg/kg) in water extracts of Sharpsburg soil incubated for 15 weeks.

microorganisms could secrete organic acids that help in dissolving gypsum and increase the concentration of SO₄²⁻ ions. Thus, these three reactions could be functioning simultaneously and affecting the concentration of SO₄²⁻ in the soil/gypsum/peat mixtures. The first two reactions (bioaccumulation of organic S and the reduction of sulfate to sulfide) seemed to be more important when the gypsum content in soil is 10 g/100 g soil or less. On the other hand, the dissolution of gypsum by organic acids seemed to be the dominant mechanism when the gypsum content in soil is above this threshold. Furthermore, the high sulfate concentrations and strong acidity, associated with high gypsum content, could enhance the dissolution process.

In general, the addition of gypsum increased the Cl⁻ concentration in the water extract (Fig. 6B). Apart from the lowest gypsum treatment (1.0 g/100 g soil), an increase in the Cl⁻ concentration was observed for all gypsum additions. This increase could be attributed to the removal of Cl⁻ ions present on the colloidal anion exchange surfaces by SO₄²⁻ ions (Sposito, 1985) and/or the dissolution of Cl⁻-containing minerals caused by the increase in soil acidity (Fig. 1A). Sumner et al. (1985) emphasized the role of anion exchange reactions in their work on soil columns. The authors found that SO₄²⁻ does not appear in the leachate until all Cl⁻ has been removed from soil. In the present study, however, we have no reasonable explanation to the decrease in the concentration of Cl⁻ as a result of the lowest gypsum addition (1.0 g/100 g soil).

Similar to other nutrients, the dissolution of Cl⁻-containing minerals and Cl⁻ added with the 5-g peat sample might explain the increase in the Cl⁻ concentration. Furthermore, it seems that the effect of peat on increasing the Cl⁻ concentration is somewhat dependent on the gypsum content in soil. The positive effect of peat on Cl⁻ concentration was enhanced by increasing the amount of gypsum in Sharpsburg soil (Fig. 6B).

Copper and Zinc

The addition of gypsum significantly decreased the concentration of copper (Cu) and zinc (Zn) in Sharpsburg soil (Figs. 7A, B). Meanwhile, increasing the rate of gypsum addition from 1 through 30 g/100 g soil did not significantly change the concentration of Cu and Zn in soil. However, as reported in Table 2, increasing the rate of gypsum from 30 to 50 g/100 g soil significantly increased the concentration of Zn (from 1,187 to 2,115 µg Zn/kg), whereas it had only a modest increase for Cu (from 17.0 to 17.8 µg Cu/kg). This increase could be attributed to the dissolution of Zn- and Cu-containing minerals as a result of the high sulfate and soil acidity (Lindsay, 1979). In their study on two calcareous soils in South Central Montana, Cates et al. (1983) found that the addition of gypsum increased soil Cu, Zn, and Mn availability and barley yield. Viator et al. (2002) indicated that gypsum addition to sugarcane grown on a silty clay loam soil in Louisiana increased Ca, S, Mn, and Zn leaf concentrations,

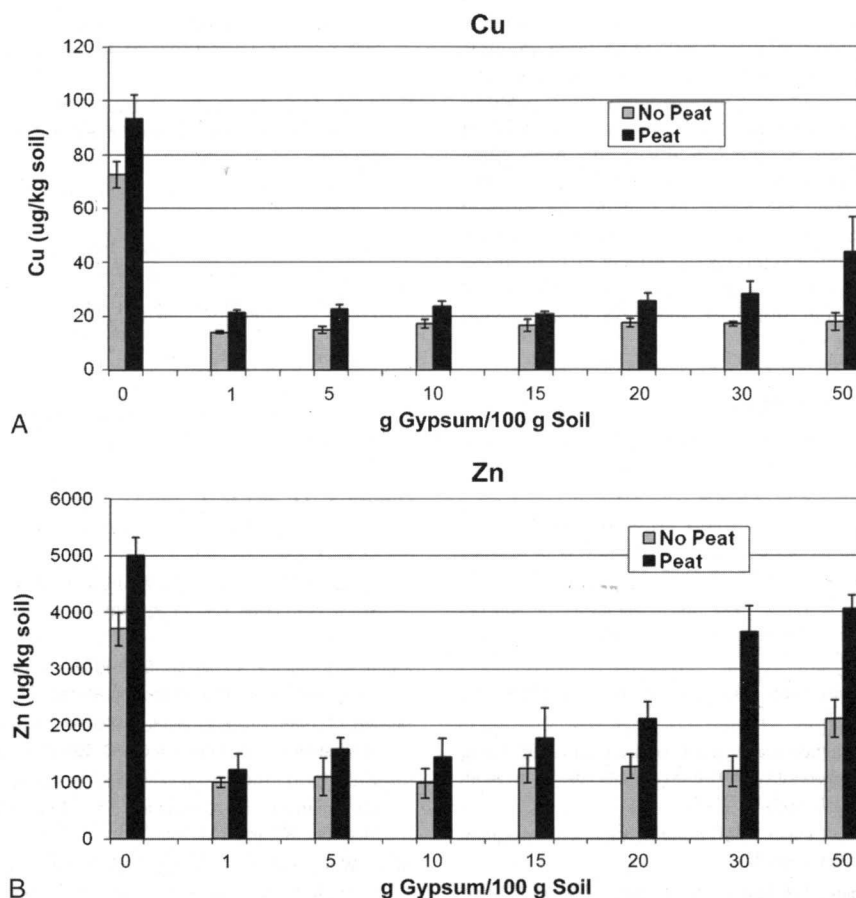


FIG. 7. Effects of gypsum and peat addition on Cu (A) and Zn (B) concentrations ($\mu\text{g/kg}$) in water extracts of Sharpsburg soil incubated for 15 weeks.

but had no effect on N, P, K, Mg, Cu, and Fe concentrations. Furthermore, Takkar and Singh (1977) found that gypsum application on alkali soils markedly decreased the soil pH and significantly increased the available soil Zn concentrations and Zn uptake by rice.

The application of peat significantly increased the concentration of both Cu and Zn in Sharpsburg soil and soil/gypsum mixtures. Similar to other nutrients, the dissolution of Cu- and Zn-containing minerals and the peat additive effect might explain the increase in the concentration of both micronutrients. Furthermore, it seemed that the effect of peat on increasing the element concentrations was somewhat dependent on the gypsum content in soil. The positive effect of peat on increasing both Cu and Zn concentrations was enhanced by increasing the amount of gypsum in Sharpsburg soil (Figs. 7A, B).

SUMMARY AND CONCLUSIONS

Understanding the effect of gypsum content on the solubility of plant nutrients is important in determining the potential productivity of gypsum-rich (gypsiferous) soils. The gypsum mineral supports high concentrations of Ca and sulfate ions in soil solution, which may negatively affect the solubility of other nutrients in soil, such as P, Fe, and Mn. Moreover, the high concentrations of Ca and SO_4^{2-} and associated salinity may have a physiological impact on root absorption sites, which reduces nutrients uptake and plant growth.

We investigated the effect of different levels of gypsum (in the presence or absence of peat) on the solubility of 13 nutrients. In a laboratory experiment, different amounts of gypsum ranging from 0 to 50 g were added to a 100-g gypsum-free soil sample (Sharpsburg Fine, montmorillonitic, mesic Typic Argiudolls), then water was added to the soil/gypsum mixtures to keep the moisture at 50% of the saturation capacity. The effect of peat was investigated in another set of soil/gypsum mixtures, where a 5-g peat moss sample was applied to each mixture, and then water was added. The soil/gypsum and soil/gypsum/peat mixtures were incubated at 32°C (90°F) for 15 weeks. After incubation, the water-extractable $\text{NO}_3\text{-N}$, P, K, Fe, Ca, Na, Mg, Mn, SO_4^{2-} , Cl, Cu, Zn, and B were determined in the mixtures.

The results indicated that the addition of gypsum increased the solubility of $\text{NO}_3\text{-N}$, K, Ca, Mg, Mn, Cl, and SO_4^{2-} , although it decreased P, Na, Fe, Cu, Zn, and B. Phosphorus was the only major nutrient that has been adversely affected by the addition of gypsum. On the other hand, the application of peat generally increased the solubility of all nutrients tested, except those of $\text{NO}_3\text{-N}$ and SO_4^{2-} . It can be concluded that the application of peat could effectively minimize the adverse effect of gypsum on P solubility and improve the solubility of most nutrients tested. Thus, the application of peat or other organic sources (i.e., animal manure and organic compost) could be recommended for gypsum-rich soils to increase its productivity.

The widely accepted negative effects of gypsum on soil fertility as well as the limited response to fertilizer application

could not be fully explained by the solubility data. We believe, however, that the physiological effects of adding large amounts of Ca and SO_4^{2-} on nutrient uptake (root absorption sites) may play an important role in reducing the productivity of gypsum-rich soils. For example, the high uptake of Ca may exert an antagonistic effect on Mg, K, and Mn absorption, even when sufficient concentrations of these nutrients are present in the soil solution. Investigating the effect of gypsum on nutrient absorption by plant roots was out of the scope of our study. Last, we conclude that understanding the effects of gypsum on both the nutrient solubility and absorption by plants would improve land management practices and help in increasing the productivity of these soils.

REFERENCES

- Carter, M. R., and J. A. Cutcliffe. 1990. Effects of gypsum on growth and mineral content of Brussels sprouts, and soil properties of Orthic Podzols. *Fertil. Res.* 24:77–84.
- Cates, R. L., V. A. Haby, E. O. Skogley, and H. Ferguson. 1983. Effects of by-product sulfuric acid on phyto availability of nutrients in irrigated calcareous, saline-sodic soils. *J. Environ. Qual.* 13:252–256.
- Coale, F. J., P. S. Porter, and W. Davis. 1994. Soil amendments for reducing phosphorus concentration of drainage water from Histosols. *Soil Sci. Soc. Am. J.* 58:1470–1475.
- Couch, E. L., and R. E. Grim. 1968. Boron fixation by illites. *Clays Clay Miner.* 16:249–256.
- Cox, J. W., J. Varcoe, D. J. Chittleborough, and J. van Leeuwen. 2005. Using gypsum to reduce phosphorus in runoff from Subcatchments in South Australia. *J. Environ. Qual.* 34:2118–2128.
- Elrashidi, M. A. and G. A. O'Connor. 1982. Boron sorption and desorption in soils. *Soil Sci. Soc. Am. J.* 46:27–31.
- Elrashidi, M. A., V. C. Baligar, R. F. Korcak, N. Persaud, and K. D. Ritchey. 1999. Chemical composition of leachate of dairy manure mixed with fluidized bed combustion residue. *J. Environ. Qual.* 28:1243–1251.
- Elrashidi, M. A., D. Hammer, C. A. Seybold, R. J. Engel, R. Burt, and P. Jones. 2007. Application of equivalent gypsum content to estimate potential subsidence of gypsiferous soils. *Soil Sci.* 172:209–224.
- Eswaran, H., and G. Zi-Tong. 1991. Properties, genesis, classification, and distribution of soils with gypsum. In W. D. Nettleton, et al. (eds.). *Properties, Characteristics, and Genesis of Carbonate, Gypsum, and Silica Accumulations in Soils*. SSSA Spec. Publ. no. 26. SSSA, Madison, WI, pp. 89–119.
- Favaretto, N., L. D. Norton, B. C. Joern, and S. M. Brouder. 2006. Gypsum amendment and exchangeable calcium and magnesium affecting phosphorus and nitrogen in runoff. *Soil Sci. Soc. Am. J.* 70:1788–1796.
- Fleet, M. E. L. 1965. Preliminary investigations into the sorption of boron by clay mineral. *Clay Miner.* 6:3–16.
- Keren, R. 1996. Boron. In G. Sposito, et al. (eds.). *Methods of Soil Analysis. Part 3-Chemical Methods*. SSSA, Madison, WI, pp. 603–626.
- Kovda, V. A. 1954. La geochemie des deserts de l'URSS. Communication au 5me Congres International de la Science du Sol. L'Academie des Sciences, Moscou.
- Larsen, S., D. Gunary, and C. D. Sutton. 1965. The rate of immobilization of applied phosphate in relation to soil properties. *J. Soil Sci.* 16: 141–148.
- Lindsay, W. L. 1979. *Chemical Equilibria in Soils*. John Wiley & Sons, New York, NY.
- Mengel, K., and E. A. Kirkby. 1982. *Principles of Plant Nutrition*. International Potash Institute, Bern, Switzerland.
- Moore, P. A. Jr., and D. M. Miller. 1994. Decreasing phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. *J. Environ. Qual.* 23:325–330.
- Nelson, P. N., E. Cotsaris, J. M. Oades, and D. B. Bursill. 1991. Organic carbon in water, its sources and role in nutrient transport. Project 86/66. Australian Center for Water Treatment and Water Quality Research, Salisbury, Australia.
- O'Brien, L. O., and M. E. Sumner. 1988. Effects of phosphogypsum on leachate and soil chemical composition. *Commun. Soil Sci. Plant Anal.* 19:1319–1329.
- Shainberg, I., M. E. Sumner, W. P. Miller, M. P. W. Farina, M. A. Pavan, and M. V. Fey. 1989. Use of gypsum on soils: A review. *Adv. Soil Sci.* 9:1–111.
- Singh, B. R., and S. N. Taneja. 1977. Effects of gypsum on mineral nitrogen status in alkaline soils. *Plant Soil* 48:315–321.
- Sposito, G. 1985. Chemical models of weathering in soils. In *The Chemistry of Weathering*. J. I. Drever (ed.). D. Reidel, New York, NY.
- Stevenson, F. J. 1991. Organic matter-micronutrient reactions in soil. In *Micronutrients in Agriculture*. J. J. Mortvedt, et al. (eds.). SSSA, Madison, WI, pp. 145–186.
- Stout, W. L., and A. N. Sharpley. 2000. Effectiveness of coal combustion by-products in controlling phosphorus export from soils. *J. Environ. Qual.* 29:1239–1244.
- Sumner, M. E., W. P. Miller, D. E. Radcliffe, and M. McCray. 1985. Use of phosphogypsum as an amendment for highly weathered soils. *Proc. 3rd Int. Phosphogypsum Symp.*, pp. 111–136. Florida Institute for Phosphate Research, Bartow, FL.
- Takkar, P. N., and T. Singh. 1977. Zinc nutrition of rice as influenced by rates of gypsum and zinc fertilization of alkali soils. *Agron. J.* 70: 447–450.
- USDA/NRCS. 2004. *Soil Survey Laboratory Methods Manual*. Soil Survey Investigations Report No. 42, Version No. 4. USDA-NRCS, Washington, DC.
- Viator, R. P., J. L. Kovar, and W. B. Hallmark. 2002. Gypsum and compost effects on sugarcane root growth, yield, and plant nutrients. *Agron. J.* 94:1332–1336.
- Zheljaskov, V. D., T. Astatkie, C. D. Caldwell, J. Macleod, and M. Grimmett. 2006. Compost, manure, and gypsum application to timothy/red clover forage. *J. Environ. Qual.* 35:2410–2418.